

PATENT BUREAU OF JAPAN
OFFICIAL GAZETTE FOR UNEXAMINED PATENTS

Japanese Kokai Patent No.: Hei 4-21573

Disclosure Date: January 24, 1992

Request for Examination: No Number of Inventions: 1 (Total of 4 pages)

<u>International Class⁵.</u>	<u>Identifying symbols</u>	<u>Intra-agency file nos.</u>
C 04 B 35/66	E	7158-4G
35/06	R	8924-4G
35/66	T	7158-4G

Title: Basic Monolithic Refractory

Application No.: Hei 2-121811

Application Date: May 12, 1990

Inventors: Keita Koyago
 c/o Nisshin Steel Co., Ltd.
 Kure Works
 11-1 Showa-cho
 Kure-shi, Hiroshima-ken

 Tadahiro Sugibayashi
 c/o Nisshin Steel Co., Ltd.
 Kure Works
 11-1 Showa-cho
 Kure-shi, Hiroshima-ken

 Tadayuki Gyotoku
 c/o Nisshin Steel Co., Ltd.
 Kure Works
 11-1 Showa-cho
 Kure-shi, Hiroshima-ken

Applicant: Nisshin Steel Co., Ltd.
 4-1, 3-chome Marunouchi
 Chiyoda-ku, Tokyo

Agent: Koichi Sato, Patent Attorney

SPECIFICATION

1. Title of the Invention

Basic Monolithic Refractory

2. Claim

A basic monolithic refractory characterized by containing 1-5 parts by weight of ultrafine silica powder per 100 parts by weight of a refractory composition made from an aggregate that employs one or two or more types among magnesia clinker, dolomite clinker, limestone, magnesiolimestone, and basic brick debris, silicate binder, and curing agent and having a CaO content of 15% or more in the fine region of 1 mm or less of the refractory textile [sic] obtained and a CaO/SiO₂ ratio of

$$6.5 \geq \frac{1 \text{ mm or less CaO content (\% by weight)}}{1 \text{ mm or less SiO}_2 \text{ content (\% by weight)}} \geq 3.5$$

3. Detailed Explanation of the Invention

Industrial Field of Utilization

The present invention relates to a basic monolithic refractory having magnesia clinker, dolomite clinker, limestone, and the like as the aggregate that is used in the blow repair of steelmaking vessels such as electrical furnaces, rotary kilns, ladles, and tandishes.

Prior Art

Blow repair of steelmaking vessels such as electrical furnaces, rotary kilns, ladles, and tandishes by a repair material made from a basic monolithic refractory is conducted periodically or as needed to prolong the life of the refractory lining. Since the repair material in such blow repair is blown in while hot at 400-1400°C, the repair material must have a high adhesion rate while hot. It also must have strong corrosion resistance to improve durability when [the vessel] receives 1500-1700°C molten steel. Basic monolithic refractories based on a phosphate binder

that has good adhesiveness while hot and actualizes high strength are consequently generally used as the repair material. Some basic repair materials based on organic binders such as phenol resin, tar, or pitch and basic repair materials based on silicate binders are also used.

Problems to be Solved by the Invention

However, the above repair materials have various problems. Specifically, basic repair materials based on phosphate binders can contaminate the molten steel with phosphorus which is harmful to the molten steel. Basic repair materials based on organic binders deteriorate because the carbon burns in an oxidizing atmosphere and adequate durability cannot be obtained. Basic repair materials based on silicate binders have low hot strength and give unsatisfactory fire resistance due to excessive wear by the molten steel and the like.

The present invention resolves the aforementioned problems and has as its object to provide a basic monolithic refractory with high hot strength that contains absolutely no phosphorus that might negatively affect the molten steel.

Means of Problem Resolution

The present inventors discovered that a basic monolithic refractory with high hot strength that contains absolutely no phosphorus harmful to the molten steel is obtained by using a silicate binder as the base and using a curing agent and ultrafine silica powder in combination with it.

Specifically, the present invention is characterized by containing 1-5 parts by weight of ultrafine silica powder per 100 parts by weight of a refractory composition made from an aggregate that employs one or two or more types among magnesia clinker, dolomite clinker, limestone, magnesiolimestone, and basic brick debris, silicate binder, and curing agent and having a CaO content of 15% or more in the fine region of 1 mm or less of the refractory textile [sic] obtained and a CaO/SiO₂ ratio of

$$6.5 \geq \frac{1 \text{ mm or less CaO content (\% by weight)}}{1 \text{ mm or less SiO}_2 \text{ content (\% by weight)}} \geq 3.5.$$

Combining the curing agent of the silicate binder and ultrafine silica powder obtains hot strength that could not be obtained by conventional basic monolithic refractories based on silicate binders and is equal to or greater than that of basic repair materials based on phosphate binders. This is believed to be because the CaO fraction of the fine region in the composition and the SiO₂ fraction in the silicate or ultrafine silica powder react and form compounds such as 3CaO·SiO₂ or 2CaO·SiO₂ at high temperature.

CaO and SiO₂ are believed to react in the same way in conventional silicate binders, but it appears that not enough 3CaO·SiO₂ or 2CaO·SiO₂ is produced to obtain high hot strength.

The present inventors believe that the composition of the fine region of 1 mm or less is closely related to the production of 3CaO·SiO₂ or 2CaO·SiO₂ to actualize hot strength in the basic monolithic refractory. They studied the relationship between the hot strength and the 3CaO·SiO₂ production index by adjusting the ratio of the 1 mm or less CaO compound and SiO₂ component by the amounts of curing agent, ultrafine silica powder, dolomite clinker, etc., added. Table 1 shows the mixtures tested and the test results. The figure shows the relationship between the hot strength and the amount of 3CaO·SiO₂ produced. As is evident from the figure, the hot strength increases and the 3CaO·SiO₂ production index rises when the weight ratio of the 1 mm or less CaO component and SiO₂ component is in the range of 3.5-6.5. Considering that the 1450°C hot strength level of a basic monolithic refractory based on a phosphate binder is 6 kg/cm² or more, it was understood that the weight ratio of the CaO component in the fine region of 1 mm or less and the SiO₂ component must be 3.5 or more and 6.5 or less. When the weight ratio of the CaO component in the fine region of 1 mm or less and the SiO₂ component is less than 3.5, the amount of 3CaO·SiO₂ produced increases, but low melting point SiO₂ compounds other than 3CaO·SiO₂ are produced because the SiO₂ component of the ultrafine silica and the like added for adjustment increases and adequate hot strength is no longer obtained. When the weight ratio of the CaO component in the fine region of 1 mm or less and the SiO₂ component exceeds 6.5, the amount of 3CaO·SiO₂ produced decreases and adequate hot strength cannot be obtained.

Table 1.

Mixture (% by weight)	A	B	C	D	E	F	G
Seawater magnesia clinker 3-1 mm	16	16	16	16	16	16	16
Synthetic dolomite clinker (B) 3-1 mm	15	15	15	15	15	15	15
Seawater magnesia clinker 1-0.3 mm	—	—	—	—	—	17	22
Synthetic dolomite clinker (A) 1-0.3 mm	37	37	37	37	37	20	15
Seawater magnesia clinker up to 0.3 mm	25	25	25	25	25	25	25
Silicate binder up to 0.1 mm	5	5	5	5	5	5	5
Curing agent up to 0.1 mm	2	2	2	2	2	2	2
Ultrafine silica powder up to 0.1 mm	0.5	1	2	5	7	1	1
CaO of 1 mm or less (%)	32.8	32.5	32.1	30.8	30.0	18.5	14.1
CaO of 1 mm or more/SiO ₂ ratio	6.7	6.1	5.1	3.5	2.9	3.7	1.9
Hot strength (kg/cm ²) 1500°C × 15 min	4.5	6.2	7.8	5.9	3.8	5.7	1.6
Hot strength (kg/cm ²) 1450°C × 15 min	5.3	6.4	8.0	6.1	4.7	6.0	2.1
Corrosion resistance (wear index)*	92	100	103	109	145	105	110

*High-frequency lining test 1700°C × 5 hours.

As can be seen from Table 1, the addition of ultrafine silica powder is effective in improving the hot strength because it reacts with the 1 mm or less CaO component and produces 3CaO·SiO₂. A suitable amount is 1-5% and it was also understood that a CaO content (% by weight) in the fine region of 1 mm or less is of 15% or more is appropriate. When the CaO content is less than 5%, the amount of 3CaO·SiO₂ produced is small and the hot strength decreases.

Natural magnesia clinker, seawater magnesia clinker, and the like can be used as the magnesia clinker employed in the present invention. Natural dolomite clinker, synthetic dolomite clinker, and the like can be used as the dolomite clinker.

No. 1 silicate solder, no. 2 silicate solder, no. 3 silicate solder, fast-melting silicate solder, and the like can be used as the silicate binder. Slaked lime, sodium silicofluoride, Portland cement, and the like can be used as the curing agent.

Practical Example 1

A basic blow repair material of composition C shown in Table 1 was used in the hot repair of a rotary kiln. A conventional basic blow repair material based on a phosphate binder was simultaneously used in hot repair for the sake of comparison.

The results are shown in Table 2. The residual surface area after four blow charges and removals was 50% or more and results equivalent to or better than those of the phosphate binder-based basic blow repair material were obtained.

Table 2.

Material		Product of the present invention Silicate binder-based basic blow repair material	Conventional product Phosphate binder-based basic blow repair material
Residual percentage (area %)	Charge 1	90	90
	Charge 2	80	75
	Charge 3	65	60
	Charge 4	50	40
Average removal temperature (°C)		1719	1702

Practical Example 2

A basic blow repair material of the composition shown in Table 1 [sic] was used in hot repair of a rotary kiln. Retreatment was performed because the phosphorus component in the molten steel rose when the amount of repair was large in the kiln end-phase when a conventional phosphate-based basic blow repair material was used. However, retreatment due to elevation of the phosphorus component was unnecessary even though the same amount of repair material was used, as shown in Table 3, when the aforementioned repair material of the present invention was used.

Table 3.

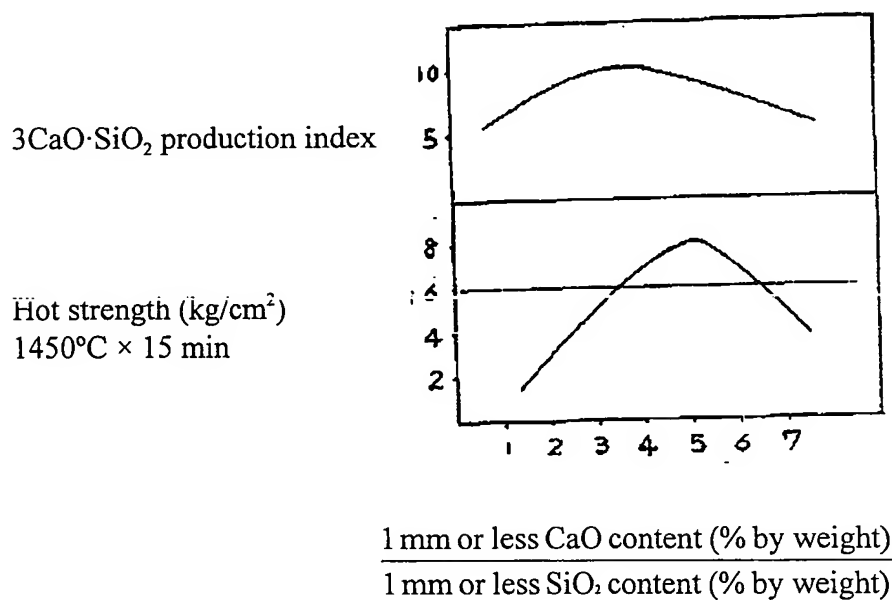
Material		Product of the present invention Silicate binder-based basic blow repair material	Conventional product Phosphate binder-based basic blow repair material
Chemical components (%)	MgO	60	60
	CaO	27	27
	SiO ₂	6	3
	P ₂ O ₅	0	3
Hot strength (kg/cm ²) 1450°C × 15 min		8.0	6.2
Hot strength (kg/cm ²) 1500°C × 15 min		7.6	4.5
Repair quantity (ton/day)		7.9	7.3
Retreatment index		0	7

Effects of the Invention

The present invention makes it possible to obtain a basic monolithic refractory with high hot strength that contains absolutely no phosphorus which is harmful to steel products. Accordingly, this makes it possible to repair steelmaking vessels by the basic refractory without any concern for contaminating the molten steel by phosphorus and also to extend the life and reduce the cost of the refractory lining of the steelmaking vessels. It also eliminates the need for retreatment associated with phosphorus contamination of the molten steel and contributes to a stable steelmaking operation.

4. Brief Explanation of the Figure

The figure is a graph that shows the relationship between the hot strength and the amount of $3\text{CaO}\cdot\text{SiO}_2$ produced.



DRUSTS ASSOCIATES
Scientific and Business Translations
P.O. Box 426, Hendersonville, NC 28793
Phone: (828) 696-0893 Fax: (828) 693-5628
E-Mail: drusts@bellsouth.net

DECLARATION OF ACCURACY AND PRECISION

Re: Translation from Japanese into English

Patent publication No. 4-21573

This declaration certifies the accuracy and precision of the translation from

Japanese into English

of the above material and is an accurate rendition of the text as it appeared in Japanese to the translator's best knowledge and belief.

[For the translator:]



Translator

December 11, 2003

Date